

NMR analysis of the transformation of wood constituents by torrefaction

T. Melkior^{a,*}, S. Jacob^{a,b,1}, G. Gerbaud^{b,2}, S. Hediger^b, L. Le Pape^{b,c}, L. Bonnefois^{b,c}, M. Bardet^{b,*}

^aCEA, LITEN, LTB, 17 rue des Martyrs, F-38054 Grenoble, France

^bService de Chimie Inorganique et Biologique, SCIB, UMR-E CEA/UJF-Grenoble 1, INAC, Grenoble, F-38054, France

^cCEA, iRTSV, Laboratoire de Chimie et Biologie des Métaux, F-38054 Grenoble, France

ARTICLE INFO

Article history:

Received 13 April 2011

Received in revised form 20 June 2011

Accepted 22 June 2011

Available online 13 July 2011

Keywords:

Biomass

Lignocellulosic fuel

Torrefaction

Wood

CPMAS ¹³C NMR

ABSTRACT

The injection of biomass in a pressurised entrained flow reactor is challenging. Biomass preparation by torrefaction before gasification could be a suitable option to improve it. Transformation of the material induced by this treatment lead to interesting features: increased brittleness, improved fluidisation properties of the powder, hydrophobicity, higher energy content. The major biomass constituents, cellulose, hemicelluloses and lignin are variously affected by torrefaction, depending on their respective reactivity. The objective of this work is to investigate the transformation of the biomass constitutive polymers induced by this thermal treatment. For that purpose, both solid-state NMR and EPR investigations have been performed on wood samples (beech) torrefied at different temperatures ranging from 200 °C to 300 °C. The results of these investigations have been compared with data obtained on untreated wood. These characterizations have brought to light different transformations of the polymers: de-acetylation of hemicelluloses, demethoxylation of lignin, changes in the cellulose structure. Furthermore, the temperature at which depolymerisation of the different components begins to occur has been identified.

© 2011 Elsevier Ltd. All rights reserved.

1. Introduction

Facing the worldwide growing demand of energy while reducing the anthropogenic greenhouse gas emissions, leads to the increasing exploitation of renewable energy sources. In this context, biomass, which is currently the fourth largest energy source in the world, appears to be a valuable resource. The conversion of lignocellulosic biomass, such as forestry and agricultural residues, into liquid fuels is currently a promising option. A possible route consists in converting biomass into a synthesis gas (mainly consisting of CO, H₂, CO₂ and H₂O) that can be used to obtain liquid fuel (thermochemical route). This process chain is commonly called Biomass to Liquids, BtL. The technology is not yet mature and many challenges have to be solved before such a process can be used on an industrial scale [1].

Among the promising technologies for biomass gasification, the entrained flow reactor seems to be particularly suitable for BtL plants. In such a reactor, biomass is fed as a fine powder, with particle size below 500 μ. This constraint is at the moment one of the major issues to be solved. Due to its fibrous structure, the size

reduction of fresh biomass is a costly and technically difficult operation. The pre-treatment of biomass by torrefaction is expected to enhance the grindability of the material and also the fluidisation behaviour of the product [2,3], which is of prime importance for its handling and injection into the gasifier. Torrefaction consists in a mild thermal treatment at a temperature ranging from 200 to 300 °C during several tenths of minutes in an inert atmosphere.

Torrefaction removes water and organic volatile components of low molecular-weight. It also induces more or less intense chemical transformations within the polymers of the cell wall, and affects the mechanical strength of the material, which becomes less fibrous and more brittle. Logically, the more severe the conditions of the treatment are (temperature or duration), the greater amount of energy is saved for grinding and the better is the fluidisation behaviour of the powder obtained after grinding [4,5]. On the other hand, the mass of organic matter lost during the pre-treatment must be kept as low as possible. Optimising the operating conditions of the treatment is therefore crucial. This requires a better understanding of the chemical and physical transformations occurring in the material. Although a lot of data are available about wood pyrolysis (treatment temperature typically higher than 300 °C), relatively little research has addressed the effect of temperature on the torrefaction process.

In the last decades, research effort has been brought to study the transformations induced by the mild heating of wood, often called retification, as a preservation treatment to replace the usual biocidal-treatments. Mild heat treatment is reported to be an effective method to improve the wood dimensional stability and its

* Corresponding authors. Tel.: +33 4 38 78 49 35; fax: +33 4 38 78 52 51 (T. Melkior), tel.: +33 4 38 78 57 72; fax: +33 4 38 78 50 90 (M. Bardet).

E-mail addresses: thierry.melkior@cea.fr (T. Melkior), michel.bardet@cea.fr (M. Bardet).

¹ Present address: Institut Technologique FCBA, Pôle Nouveaux Matériaux, 38044 Grenoble, France.

² Present address: CNRS, Bioénergétique et ingénierie des protéines (UPR 9036), 31 Chemin Joseph Aiguier, F-13402 Marseille, France.

durability, since the hygroscopicity of the material is reduced [6–9]. However, the conditions of the treatment, such as the composition of the atmosphere, the temperature range and the duration, differ from the ones envisaged for torrefaction in the context of a BtL plant, since the objectives are different. In particular, keeping the mass loss of the solid as low as possible is one of the major goals in gasification processes, whereas it does not have to be optimised for the production of “high-value” materials. On the contrary, the reduction of the mechanical strength of the material is the result expected from the preparation of the biomass before its injection in a gasifier, while it is a major drawback if one intends to improve the wood durability. The temperature range for wood retification lies typically between 150 and 250 °C, while it is between 230 and 300 °C for wood torrefaction. The duration of the treatment is several minutes to 1 h for wood torrefaction, while it can be of several hours in wood retification.

Wood cells are composed of cellulose microfibrils coated with hemicelluloses. Lignin is deposited in between the microfibrils, and sometimes within the amorphous regions of the microfibril. The wood components exhibit different behaviours under mild thermal treatment. Over the temperature range of interest, the most reactive components are hemicelluloses. The thermal decomposition of xylan, one of the most important components of hardwood hemicelluloses, is observed to begin around 200 °C, with high weight losses [10]. The degradation of xylan in the considered temperature range can be represented as a two-stage mechanism. The first step starts around 200 °C and is very fast, while the second slower stage is observed for temperatures higher than 270 °C [11]. The lignin degradation starts at temperatures above 200 °C, with a slower kinetics than for the hemicellulose degradation [12]. Cellulose is the most stable component over the temperature range considered here; its thermal degradation starts around 270 °C, with a quite slow kinetics [10], which accelerates noticeably at more elevated temperatures, typically above 300 °C. At last, wood also contains extractives (resins, tannins, etc.) in variable proportions. A significant part of them are volatilised when the material is heated and their content is reduced after thermal treatment [13,14].

Previous investigations of pyrolysis char residues with ^{13}C NMR and EPR have demonstrated that these techniques are able to give relevant insights into the structure of thermal treated lignocellulosic materials [15]. CPMAS ^{13}C NMR has also been used to characterise the degradation of wood submitted to a mild thermal treatment [8,16,17]. The major conclusion obtained from solid-state NMR in previous studies is the extent of degradation taking place within the different wood components. Hemicelluloses appear to be the most degraded component, when the treatment temperature exceeds 240–260 °C. Cellulose crystallinity is known to be increased by a heat treatment above 200 °C. Modifications affecting lignin have also been noticed, but to a lesser extent. This polymer appears to be the most stable, although crosslinking reactions were observed above 260 °C. These cross-linking reactions may act as a reinforcing factor occurring into the wood. They are believed to improve the hygroscopicity and the dimensional stability of wood [6]. These last results seem to be in contradiction with those obtained by Bergman et al. [2] with thermo gravimetric analyses (TGA), but it has to be considered that first they were carried out on isolated components of wood and second the experimental conditions are difficult to compare.

The objective of this work is to perform ^{13}C NMR and EPR characterisations of wood samples, which were heat treated under the conditions representative of the biomass treatment by torrefaction, before upgrading by gasification. The main interest of high-resolution solid-state NMR spectroscopy lies in the possibility to observe the concomitant chemical transformation of the main wood components in a resolved manner.

2. Material and methods

2.1. Torrefaction

The equipment used to carry out the torrefaction step is represented in Fig. 1. It consists of a tube, of 270 mm in height and 25 mm in diameter, swept by pre-heated nitrogen (see Fig. 1). The gas-flow rate, ranging from 0.5 to 3 NL/min, was controlled by mass-flow rate regulators (Brooks Instrument). Five to six wood samples were disposed inside this tube, on a porous plate. The tube was introduced within an oven, type Nabertherm RT 50–250/13, 2 kW. Nitrogen sweeping was used to maintain an inert atmosphere, to carry the volatile products, and to heat the biomass samples.

The temperature at the core of one of the wood samples was recorded with a K-type thermocouple (0.5 mm in diameter). In some tests, the gas composition was measured online with a micro gas chromatograph coupled with thermal conductivity detectors (Agilent 3000A). In this study, the compounds detected with this apparatus were H_2O , CO , CO_2 and methanol. The mass loss of the samples was obtained by weighting the samples before and after the treatment. Ultimate analysis of the wood after torrefaction were performed in a testing laboratory; C and H were quantified with an Elementar Vario Microcube apparatus and O by IR-thermoconductivity.

The wood samples used in this work were cylindrical pieces (diameter: 5 mm–Height: 15 mm) cut in a beech trunk. They were previously oven dried at 105 °C during 24 h, and then stored under dry conditions (desiccator containing silica-gel salt). This dried wood corresponds to the raw sample used as reference throughout this study. The torrefaction protocol was the following: the raw samples were placed inside the tube swept by nitrogen, which was itself introduced within the oven at ambient temperature. The oven was then turned on, and it rapidly (~some minutes) reached the working temperature. In a first step, the sample temperature increased regularly, before it reached a plateau (see Fig. 2). The durations of the transient step and the plateau were respectively ~60 and 50 min. Note that during the “plateau step”, the sample temperature could not be thoroughly stabilised: it slightly but regularly increased, with variations ranging from 4 to 8 °C.

2.2. Characterisation of the wood samples

2.2.1. Solid-state NMR experiments

Standard ^{13}C NMR experiments and 2D ^1H – ^{13}C NMR correlation spectra of the raw and treated wood samples were performed. The samples were previously gently grinded to ensure their homogeneity.

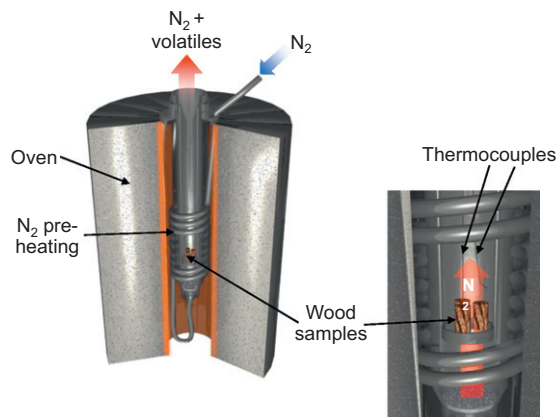


Fig. 1. Reactor used to perform wood torrefaction. Picture on the right is an enlargement of the reactor centre containing the samples to be torrefied.

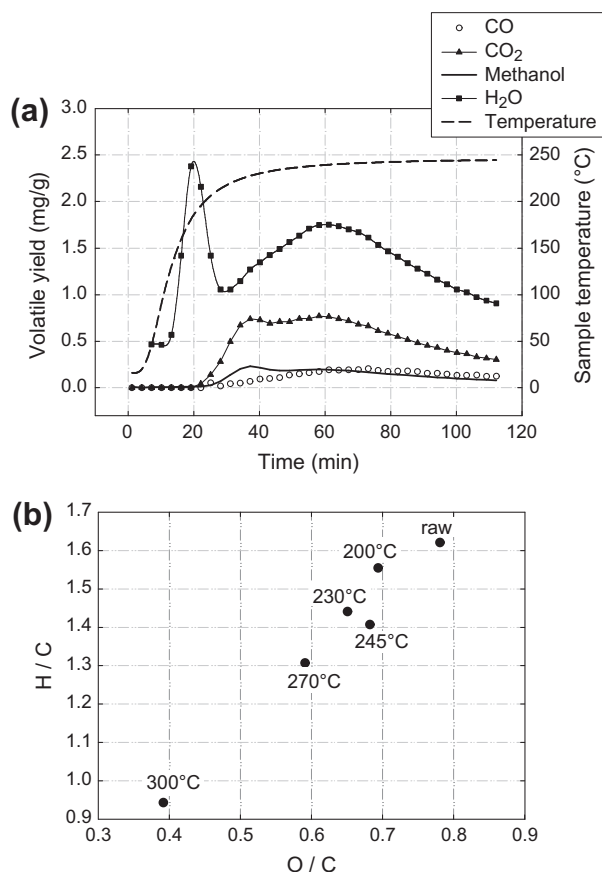


Fig. 2. (a) Time history of the sample temperature (dashed curve) and of volatiles formed during the torrefaction of beech samples at a temperature of 245 °C (CO: circles, CO₂: triangles, methanol: straight line, water: squares); (b) Elemental analyses of raw and torrefied wood samples plotted in a Van Krevelen type diagram. Torrefaction temperature used for the different samples is given next to each point. The point labelled “raw” corresponds to the reference wood sample (dried at 105 °C).

2.2.1.1. Standard carbon solid-state NMR experiments. All 1D NMR experiments were carried out at room temperature with a BRUKER AVANCE DSX 200 MHz spectrometer, operating at a proton frequency of 200.13 MHz (carbon frequency at 50.3 MHz). Carbon 1D spectra were acquired with a 7 mm Bruker CPMAS probehead, using the combination of cross-polarisation (CP), magic angle sample spinning (MAS) and high-power proton decoupling methods. The magic-angle spinning speed was set to 5000 Hz. A ¹H radio-frequency field strength of 70 kHz and 87 kHz was used for proton pulses (90°-pulse duration of 3.6 μs) and proton dipolar decoupling, respectively. The ¹³C radiofrequency field strength was set to match the Hartman–Hahn condition during CP. For each spectrum, 16,384 transients were accumulated with a CP contact time of 1 ms and a recycle delay of 4 s. The chemical shift values were calibrated indirectly with the glycine carbonyl signal set to 176.03 ppm relative to tetramethylsilane (TMS). The TOSS experiment was used to record spinning-sideband-free spectra [18]. Interrupted decoupling experiments were performed by introducing in the CP experiment a 70 μs delay without decoupling before the acquisition period [19]. The corresponding spectra are not presented in this work although they were worthwhile in the assignment of spectra. In order to obtain quantitative data from the CPMAS experiments, all the integrals were corrected by a factor taking into account the dynamics of the ¹³C magnetisation build-up during the proton-to-carbon cross polarisation step [20].

A major difficulty in the interpretation of wood NMR spectra arises from signal overlapping. To circumvent this problem, decomposition of the spectra was required. It was performed with DIMFIT software, developed by Massiot et al. [21]. Based on the signal assignment, the NMR spectrum of raw wood was first fitted. The NMR-signal parameters (linewidth, chemical shift) were then used as input data to decompose the NMR spectra of torrefied samples. Additional signals were introduced if necessary to take into account the occurrence of new chemical structures.

To compare CPMAS spectra recorded under identical conditions and then have access to semi-quantitative information, the integrals were normalised by:

- The mass of sample used to fill the rotors.
- The initial mass of raw wood before torrefaction. This factor puts into evidence the loss of signal induced by the thermal treatment: if the torrefaction has more specifically affected one of the wood components (typically hemicelluloses), the proportion of the other components in the sample automatically increases (for a constant sample weight), although they may also have been affected. Thus, the peak area divided by the initial mass of raw wood remains constant as long as the structure of the considered atom is unchanged and this value decreases when the treatment has induced structural modifications.

To summary, the normalised areas were obtained by:

$$\text{“normalised peak areas”} = \text{peak area} \times (1 - \Delta m) / m_{\text{rotor}}$$

where Δm is the relative mass loss of the sample during torrefaction and m_{rotor} is the sample weight (in the NMR rotor).

2.2.1.2. ¹H–¹³C NMR correlation experiments. The 2D ¹H–¹³C HETCOR experiments were recorded at room temperature using a 4 mm Bruker CPMAS probehead on a Bruker AVANCE DSX 400 spectrometer operating at 100.62 MHz for the ¹³C and at 400.13 MHz for protons. Data were collected with 35 complex data points in the ¹H indirect dimension and 836 data points in the ¹³C dimension. The corresponding spectral widths were 23.6 and 30 kHz, respectively. For each t_1 increment, eight scans were accumulated, except for the wood sample torrefied at 300 °C where 384 scans were added. The recycle time was set to 3 s. For the cross-polarisation step, a ramped rf field centred at a strength of 72 kHz was applied on protons and the rf-field strength on carbons was adjusted to fulfil the Hartmann–Hahn condition. The proton decoupling-field strength was set to 90 kHz, both during the indirect detection with FSLG homonuclear decoupling [22], and during the direct acquisition with SPINAL heteronuclear decoupling [23]. The spinning frequency was 12 kHz and the contact time for the cross-polarisation step 100 μs. Quadrature detection in ω_1 was achieved using States-TPPI. Exponential line broadening of 100 Hz and 30 Hz was applied to proton and carbon dimensions, respectively, prior to Fourier transform.

2.2.2. EPR experiments

EPR measurements were performed with a Bruker EMX X-band continuous-wave spectrometer equipped with a Bruker ER-4116 DM cavity. Experiments were carried out at room temperature (292 K) with a microwave power from 0.2 to 200 μW and a modulation amplitude ranging from 0.3 mT to 1 mT, adjusted to record spectra containing narrow lines and broad lines, respectively. Powder samples were contained in caped synthetic Suprasil-quartz EPR tubes under argon. Radical spin quantifications were obtained using the Bruker weak pitch as a rough “standard”. The absolute quantification of species was performed by comparing the EPR signals of the weak pitch, for which the concentration of radicals is

known. Quantification was obtained after double integration of EPR signals on a defined amount of sample.

3. Results

3.1. Torrefaction process

Torrefaction of wood samples at different temperatures, 200, 230, 245, 270 and 300 °C, has been investigated. As an example, Fig. 2a shows the sample-temperature and gas-release evolution during the heat treatment performed at 245 °C. A time of 60 min was necessary for the sample temperature to reach the plateau value (see Section 2.1), where it was kept for additional 50 min. If one considers that molecular reactions due to torrefaction begin to occur as soon as the sample temperature exceeds 200 °C, the duration of the torrefaction is then approximately 95 min. The same trend is observed for measurements performed at the other above mentioned temperatures.

The temperatures of the gas sweeping the tube and of the tube wall itself have been systematically monitored during the treatment of the wood samples. Their profiles (not included in Fig. 2a) are perfectly parallel to the evolution of the temperature at the core of the wood samples. This indicates that the heat transfer inside the wood is fast in comparison with the heating of the system itself. In other words, the temperature gradient inside the wood samples is negligible, and it can be assumed that the samples are isothermal. Moreover, the energy absorbed or produced by chemical reactions does not seem to affect the temperature measured inside the wood cores.

Gas and volatile yield during the heat treatment has been monitored as well. As shown in Fig. 2a, water release is observed as soon as the sample temperature exceeds 120 °C. This corresponds to constitutive water that was not removed after drying the wood samples at 105 °C. This water is known to be linked to the macromolecules of the wood, mainly cellulose and hemicelluloses, and requires an excess of energy to be evaporated and released from the material. When the sample temperature reaches 200 °C, CO₂ is detected as well. Since this gas is produced by chemical reactions acting on the wood components, it can be concluded that material degradation under the considered thermal conditions starts to occur above 200 °C. Besides CO₂, the other gaseous products detected by µGC are CO and methanol. These latter components are observed later than CO₂, when the sample temperature reaches ~230 °C.

The mass losses of the wood samples treated at different temperatures and the results of their C, H, N elemental analysis are reported in Table 1. C, H, N analyses have been repeated four times. Mean values as well as absolute deviations are given in Table 1. Oxygen analysis was done once. Results from the elemental analysis are plotted on a van Krevelen-type diagram in Fig. 2b. The observed tendency agrees with other data from the literature [24]: the thermal treatment leads to an increase of the carbon content and to a decrease of both the hydrogen and the oxygen contents.

Table 1

Elemental analysis and mass loss of raw (dried) and torrefied wood samples. Values in parentheses are the absolute deviations observed for repeated analysis.

	Elemental analysis				Mass loss (%w)
	C (%w)	H (%w)	O (%w)	N (%w)	
Raw	46.1 (0.6)	6.2 (0.1)	48.0	0.1 (0.05)	–
Tor. 200 °C	47.1 (0.2)	6.1 (0.05)	43.6	0.2 (0.05)	0.2
Tor. 230 °C	49.5 (0.1)	5.9 (0.05)	42.9	0.1 (0.05)	7.2
Tor. 245 °C	50.1 (0.2)	5.9 (0.1)	45.6	0.2 (0.1)	13.0
Tor. 270 °C	52.8 (0.1)	5.7 (0.05)	41.6	0.2 (0.05)	24.2
Tor. 300 °C	64.4 (0.1)	5.1 (0.05)	33.6	0.2 (0.05)	44.4

The van Krevelen diagram reveals a gap between the wood samples torrefied at 300 °C and those treated at lower temperatures. This gap is also observed, as shown in Table 1, in the evolution of the mass losses as a function of the treatment temperature. Clearly, torrefaction at 300 °C leads to much more degraded materials compared to lower temperature treatments. This will be further discussed in this article.

3.2. High-resolution solid-state NMR

3.2.1. General considerations

¹³C CPMAS spectra of wood samples present signals corresponding to all the different carbons of the main wood components, i.e. lignin, cellulose and hemicelluloses, the structure of which is given in Fig. 3. A typical ¹³C CPMAS spectrum of raw (dried) wood is given in Fig. 4, spectrum A. General assignment of the signals, summarised in Table 2, relies on the results of many studies that represent a large amount of work over the last decades [25–27]. The general method used to assign the signals is thoroughly described in a recent review article [28]. Only the main features of the NMR spectra are reminded hereafter. At 21 ppm, the signal #16 is assigned to the CH₃ carbons of the hemicelluloses acetyl units. In the interval ranging between 60 and 105 ppm, large signals prevail (#8 to #14), which are predominantly assigned to cellulose, and to a lesser extent to hemicelluloses carbohydrates. Of particular interest are the signals #9 and #10, at 88.7 ppm and 83.8 ppm respectively, assigned to the C-4 of cellulose allomorphs. The signal at 83.8 ppm is indicative of either amorphous or disordered cellulose at the surface of crystalline microfibrils, whereas the signal at 88.7 ppm refers to crystalline cellulose. These signals overlap those belonging to different aliphatic carbons of lignins. In this area, the only signal which can be specifically assigned to lignins is the resonance #15 at 55.7 ppm, due to methoxy groups occurring in aromatic units. The intense signal #8 at 104.8 ppm is assigned to the C-1 of cellulose, although some overlapping with aromatic carbons of lignins cannot be excluded. A broad and weak shoulder, noted #8', at the low-frequency side of signal #8 can be assigned to the C-1 of hemicelluloses, the broadness of this signal being clearly imputable to their amorphous structure. The peaks occurring in the region between 105 ppm and 160 ppm are specific of carbons from aromatic units of lignin. The signal #2 at 152.6 ppm is classically assigned to C-3 and C-5 of syringyl units involved in β-O-4 structures. On the low-frequency side of the previous signal, the shoulder #3 is mainly assigned to the same carbons, but in non-etherified structures. The relative intensities of these two broad signals allow us to estimate the depletion of the β-O-4 linkages inside the lignin polymers. The signal #1, at 172 ppm, is generated by the carbonyls of hemicelluloses acetoxy groups, although it could also be due to acid groups occurring in wood.

3.2.2. Qualitative analyses of torrefied woods

In the spectra of torrefied wood presented in Fig. 4 spectra B to F, two temperature regimes (below and above 270 °C) can be distinguished. Up to torrefaction temperatures of 270 °C (spectra B to E) qualitative changes in the NMR spectra can be evidenced only after a very close inspection of the signals. To better highlight the evolutions caused by the thermal treatment, spectra A to E are normalised by the intensity of the signal of cellulose C-1 (signal #8 at 104.8 ppm), which is assumed to be unchanged over this range of temperature.

The depletion of hemicelluloses is clearly indicated by the decrease of its typical acetyl signals #1 and #16 at 172 ppm and 21 ppm, respectively. Another interesting feature that can be noticed in Fig. 4 is the behaviour of signal #8' assigned to hemicelluloses C-1 that unambiguously vanishes as the temperature

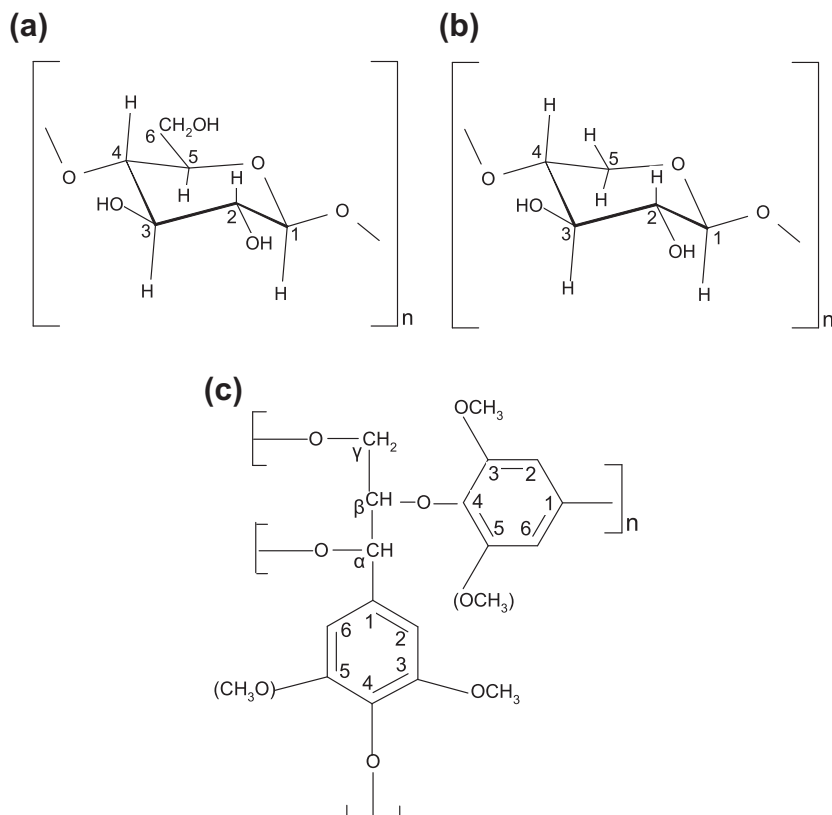


Fig. 3. Schematic representation of the main components of wood: (a) cellulose, (b) xylan (main component of hemicelluloses), (c) lignin. Hemicelluloses acetyl groups ($-\text{OOC}-\text{CH}_3$) are not shown in (b) since the O-acetyl substitution can occur at any of the hydroxyl position in xylan. Structure (c) corresponds to a syringyl dimer. Replacement of the methoxyl groups $-\text{OCH}_3$ given in parenthesis by a hydrogen atom leads to the guaiacyl structure.

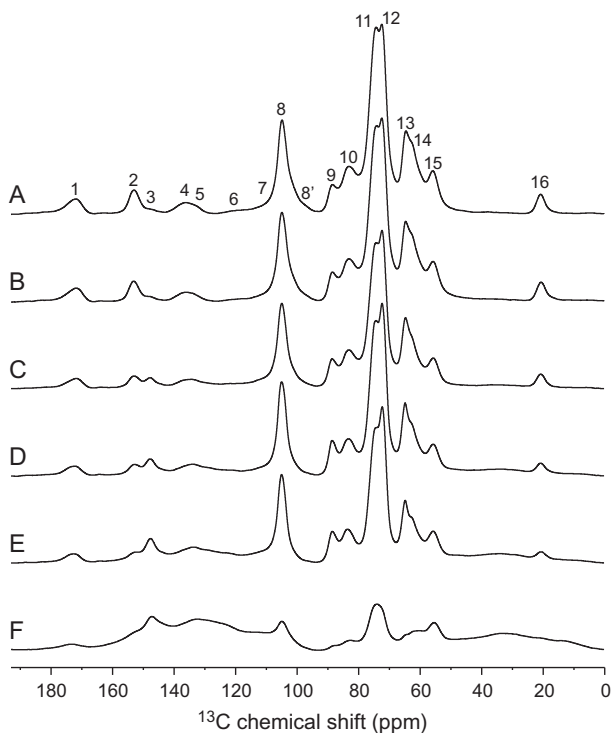


Fig. 4. 50 MHz ¹³C CPMAS high-resolution solid-state NMR spectra of raw and torrefied samples of beech wood. A: raw wood (dried at 105 °C), B–F: wood torrefied at 200 °C (B), 230 °C (C), 245 °C (D), 270 °C (E), and 300 °C (F). In spectrum A, the peaks are numbered from 1 to 16 and the corresponding assignment can be found in Table 2.

increases. This demonstrates the sensitivity of hemicelluloses to torrefaction.

Another striking feature of these spectra is the changes that can be observed for signals #2 and #3 assigned to syringyl C-3 and C-5 in etherified and in non-etherified β -O-4 structures, respectively. The decrease observed for resonance #2 can either be due to the depolymerisation of lignins by cleavage of the β -O-4 bonds, or to the demethoxylation of syringyls, becoming thus guaiacyl units. Demethoxylation could explain most of this change since signal #15, assigned to methoxyl groups, decreases as the temperature increases. By observing signals #4 and #5 one can conclude that up to 230 °C the cleavage of β -O-4 bonds is not an important route since it is not possible to observe any significant decrease in the signal #4, which is assigned to both syringyls and guaiacyls included in such structures. On the contrary, at higher treatment temperatures (245 °C and above) the tendency of the relative intensity of signal #4, which decreases, and of signal #5, which increases, is a strong indication of β -O-4 bonds cleavage.

As already mentioned, the spectrum of wood torrefied at 300 °C (spectrum F in Fig. 4) differs markedly from those obtained at lower temperature conditions. Indeed, all the signals assigned to cellulose decrease drastically. Furthermore, broad aromatic and aliphatic signals, centred at 128 ppm and 32 ppm respectively, can be observed. The broadness of these new signals indicates that the corresponding carbon types are found in different chemical environments across the sample. Their chemical formation has been extensively discussed for lignocellulosic material and their isolated components treated at much higher temperature, 500 °C for instance [29–32]. In the spectra of Fig. 4, resonances corresponding to such units start to appear for samples treated at 250 °C (spectrum D) and above, but their intensities remain low.

Table 2

Resonance assignment of ^{13}C CPMAS spectrum of raw wood, given in Fig. 4 (spectrum A).

Resonance number	Chemical shift (ppm)	Assignment
1	172	Hemicelluloses: $-\text{COO}-\text{R}$, $\text{CH}_3-\text{COO}-$
2	152.6	Lignin: S-3(e), S-5(e)
3	148–147	Lignins: S-3(ne), S-5(ne), G-3(ne, e), G-4(ne, e)
4	138–138.5	Lignins: S-1(e), S-4(e), G-1(e)
5	134–133	Lignins: S-1(ne), S-4(ne), G-1(ne)
6	121	Lignin: G-6
7	114–106	Lignins: G-5, G-6, S-2, S-6
8	104.8	Cellulose: C-1
8'	104–101	Hemicelluloses: C-1
9	88.7	Carbohydrates: C-4 cellulose (ordered)
10	83.8	Lignins: C β Carbohydrates: C-4 cellulose (disordered)
11	74.8	Lignins: C α Carbohydrates: C-2,-3,-5
12	72.2	Carbohydrates: C-2,-3,-5
13	64.7	Carbohydrates: C-6 cellulose (ordered)
14	61.6	Lignins: C γ Carbohydrates: C-6 cellulose (disordered)
15	55.7	Lignins: OCH_3
16	21	Hemicelluloses: $\text{CH}_3-\text{COO}-$

Abbreviations; S: carbon in syringyls (aromatic unit with two methoxyl groups), G: carbon in guaiacyls (aromatic unit with only one methoxyl), ne: in non-etherified arylglycerol β -aryl ethers, e: in etherified arylglycerol β -aryl ethers.

3.2.3. Quantitative analyses of NMR data

In order to secure the previous qualitative observations, quantitative analyses of the NMR spectra were carried out. For cellulose and hemicelluloses, the focus was set on resonances arising from the following carbon atoms:

- C-1 of cellulose and hemicelluloses (signal #8).
- C-4 of cellulose in ordered and disordered/amorphous cellulose (signals #9 and #10, respectively); their sum gives the total amount of C-4 in cellulose.
- C-6 of cellulose (signal #13).
- Carbonyl and methyl carbons of acetyl groups in hemicelluloses (signals #1 and #16, respectively).

In the same way, the following carbons are used to characterise the modifications in the lignin structure:

- C-3 and C-5 of syringyls in etherified (signal #2) and non-etherified structures (signals #3). Signal #3 also contains contribution of C-3 and C-4 of guaiacyls in etherified and non-etherified structures.
- Carbon atoms of methoxyl groups (signal #15).

Evolution of signals assigned to the carbons of hemicelluloses acetyl groups (carbonyl and methyl carbons) as a function of torrefaction temperature is given in Fig. 5a. Both curves have a similar behaviour indicating that hemicelluloses start to lose acetyl groups at a torrefaction temperature above 200 °C. Fig. 5b shows that the amount of C-1, assigned to both cellulose and hemicelluloses clearly drop as well, starting around 245 °C. This decrease appears at lower temperature than for C-4 and C-6 resonances, which are mainly assigned to cellulose. This reflects degradation of hemicelluloses moiety. According to the evolution of C-4 resonances, cellulose degradation is clearly observed above 245 °C.

It is well established that the C-4 atom in the cellulose structure gives rise to two resonances, which are characteristic of the structural molecular organisation inside the fibrils, for instance crystalline or amorphous state of cellulose. The variations of these signals are plotted as a function of the torrefaction temperature in Fig. 5c. It brings to light that there is an initial increase of the signal corresponding to crystalline cellulose in the range from 200 to 245 °C. This feature indicates that amorphous (or disordered) cellulose is partly re-crystallized due to thermal treatment in this temperature range, before being degraded at higher temperatures.

Concerning lignin degradation, data are reported in Fig. 5d. It clearly appears that the signals from C-3 and C-5 of syringyl units in etherified structures and the one from methoxyl carbons exhibit similar evolutions. They are stable up to 200 °C and then start to degrade markedly. This could indicate that demethoxylation is actually the dominant mechanism above 200 °C. Demethoxylation of syringyls is expected to lead to an increase of guaiacyls which contribute to signal #3. Indeed, above 200 °C, the integral of signal #3 (C-3 and C-5 of syringyls in non-etherified structures and guaiacyls C-3 and C-4) evolves exactly in an opposite way from the two others. This confirms that the decrease in the C-3 and C-5 of syringyls in etherified β -O-4 structures is mainly due to the demethoxylation of only one position of syringyls (C-3 or C-5), leading to etherified guaiacyls. It is to note that the symmetric behaviour observed for the signal #2 (or #15) and signal #3 also indicates that guaiacyl units are not significantly affected by demethoxylation up to a temperature of 245 °C. Above 245 °C, the curve of signal #3 reaches a plateau that may indicate that demethoxylation begins to occur in guaiacyl units. This is supported by the fact that the signal of methoxyl groups (signal #15) still decreases.

The similar slope of the decrease in signal #2 from C-3 and C-5 of syringyl units in etherified structures and of signal #15 from methoxyl groups shows surprisingly that in this temperature range, the cleavage of β -O-4 bonds is not the predominant chemical route, although it still occurs to some extent above 245 °C, as mentioned in the previous section from the behaviour of signals #4 and #5 in Fig. 4. The major reaction is demethoxylation, which preferentially affects only one methoxyl group of the syringyl units.

3.2.4. Results from 2D ^1H - ^{13}C solid-state NMR spectra

As mentioned previously, the overlapping of NMR signals, especially for torrefied samples, can make their assignment questionable. Hence the relevance of the interpretation has to be ensured, in particular for cellulose, considering the importance of this component.

Results obtained on three significant samples, crude cellulose from SIGMA and wood samples torrefied at 270 °C and 300 °C, are compared in Fig. 6 over the spectral range between 140 and 20 ppm, which is mainly assigned to the cellulose moiety. 2D spectra of raw wood and wood samples treated at temperatures below 270 °C were also recorded, but are not reported in Fig. 6. Over this spectral range, they are all similar to the spectrum B of the wood sample torrefied at 270 °C. Up to torrefaction temperature of 270 °C, the NMR resonance pattern of residual wood cellulose (spectrum B) and pristine cellulose (spectrum A) are alike. It indicates that signal intensity in the spectral region from 110 to 60 ppm is dominated by cellulose signals. Interpretation of the data in terms of slight structural changes in cellulose is therefore meaningful. It is clear that after a treatment temperature of about 300 °C the pattern of cellulose signals is drastically modified. As an example, signal #13 of C-6 in ordered or crystallised cellulose has completely vanished out. On spectrum C, new broad signals centred at 128 ppm and 32 ppm are clearly visible and were already commented in the qualitative analyses of the 1D spectra. From

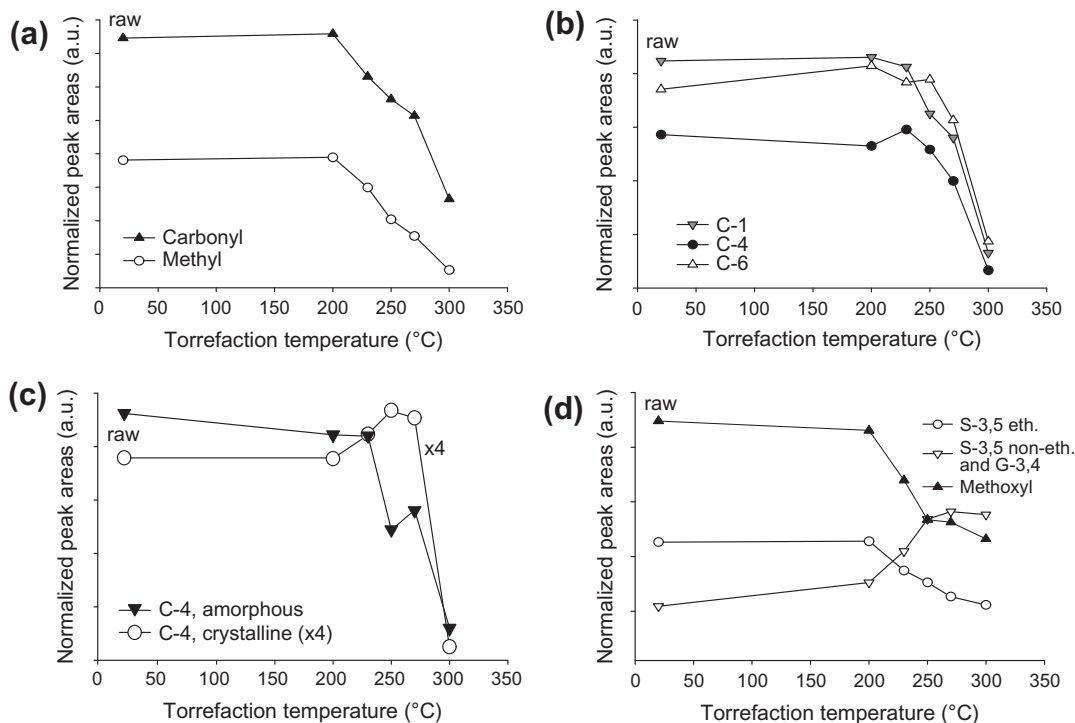


Fig. 5. Evolution of different ^{13}C NMR signal integrals as a function of the torrefaction temperature: (a) hemicelluloses signals #1 (carbonyl, triangles) and #16 (methyl, circles); (b) cellulose signals #8 (C-1, grey triangles), sum of #9 and #10 (C-4, black circles), and #13 (C-6, white triangles); signal #8 also contains contribution from hemicelluloses C-1; (c) C-4 cellulose signals #9 (crystalline cellulose, circles) and #10 (amorphous cellulose, triangles); (d) lignin signals #2 (etherified syringyls, circles), #3 (non-etherified syringyls, guaiacyls, white triangles), and #15 (methoxyl, black triangles). Points at 20 °C (labelled “raw”) correspond to the reference dried raw wood. In (c) the peak-area intensities of the crystalline C-4 resonance have been enhanced by a factor 4 compared to the amorphous C-4 intensities.

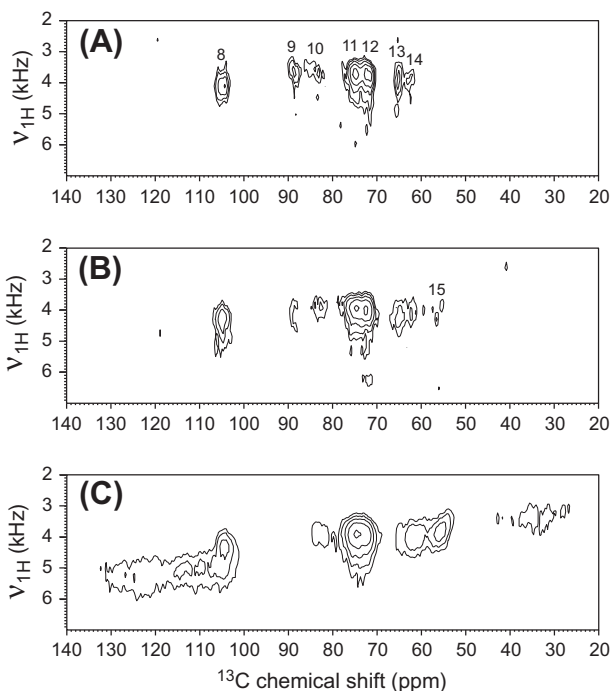


Fig. 6. 2D ^1H – ^{13}C HETCOR spectra of crude cellulose (A) and wood samples torrefied at 270 °C (B) and 300 °C (C). For all spectra, only the region between 140 and 20 ppm is displayed. Numbering of peaks in A and B corresponds to the assignment of 1D spectra of Fig. 4 and Table 2.

their proton chemical shifts, it can be concluded that they are not bound to any oxygen atom. These aromatic and aliphatic structures were shown to be formed from the thermal degradation of sugars,

which lead to polymers of hydroxymethyl furfural derivatives as shown by Baccile and coworkers [29].

3.3. EPR measurements

EPR spectroscopy allows the measurement of residual radical concentration in the different samples, although it should be reminded that radicals are often by nature unstable compounds. Their concentration in torrefied wood gives indications about the extent of the chemical transformations caused by the heat treatment. From the changes in shape and g -values observed in Fig. 7a, it clearly appears that these transformations are chemically temperature dependant, which undoubtedly plays an important role both in the degradation of wood components and in the recombinant reactions of the products. The amount of residual radicals in wood samples torrefied at temperatures above 200 °C increases exponentially as shown in Fig. 7b. In addition, the samples appear to be more and more sensitive to micro-wave power saturation as the torrefaction temperature increases (for the sample torrefied at 300 °C, the radical signal was still saturated even at a micro-wave power of 0.2 μW). For torrefied samples (torrefaction temperature between 200 and 300 °C) the peak-to-peak line width of the EPR line decreases linearly as a function of the torrefaction temperature. For the same temperature range, the g -value decreases linearly as well, and linear regression gave $g = 2.007(1) - 1.4(4) \cdot 10^{-5} \cdot T$. Such a linear behaviour of the g -value has already been observed in archaeological or recent charred wood [33]. The slope is similar to the previously published one ($-10^{-5} \text{ } ^\circ\text{C}^{-1}$), and differences in g -values may have two explanations. Firstly, the nature of wood is different in both studies: beech in the present study compared to white oak in Triantafyllou's publication [33]. Secondly, the heating procedure differs as well, with a heat treatment in an oven and under inert atmosphere in

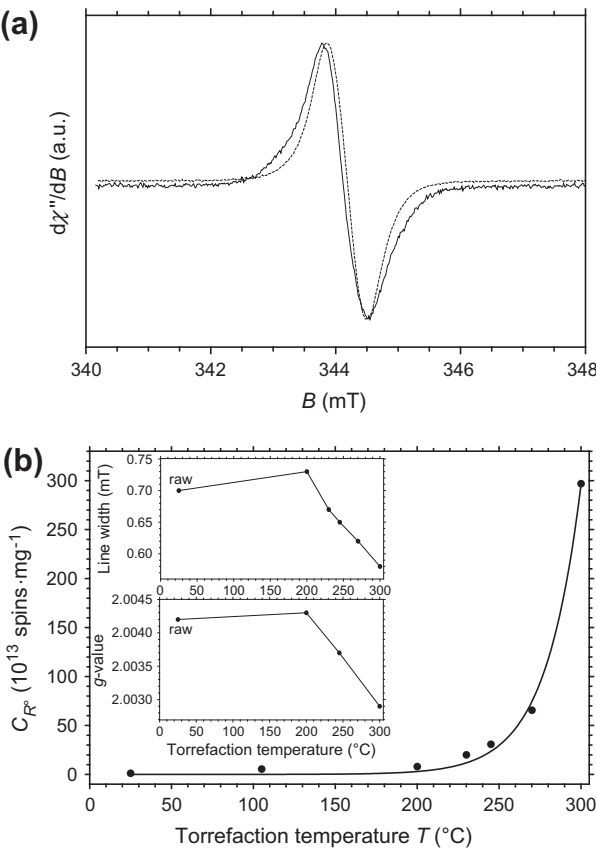


Fig. 7. (a) EPR spectra at room temperature of wood samples torrefied at 200 °C (straight line), and at 245 °C (dotted line), normalised at the same height for line-width comparison. Following experimental conditions were used for both spectra, respectively: sample amount of 102.2(1) mg and 95.7(1) mg, microwave frequency of 9.653 GHz and 9.652 GHz, microwave power of 50 μ W and 13 μ W. In both cases, the modulation frequency was set to 100 kHz, the modulation amplitude to 0.3 mT, the time constant to 21 ms, and the number of scans to 1. (b) Amount of free radicals measured with EPR spectroscopy in wood samples as a function of torrefaction temperature. The straight line represents the best exponential fit of the data points and gives a radical concentration function of $C_R(T) = 0.0003(2) \cdot \exp[0.046(3) \cdot T]$. In the insets are given the evolution of the peak-to-peak line width (upper inset) and of the g-value (lower inset) as a function of the torrefaction temperature. Points labelled “raw” correspond to the reference wood sample (dried at 105 °C).

the present study against direct burning in Traintafyllou’s work [33]. These observations confirm the results of the NMR analyses: above 200 °C, the chemical transformations induced by the thermal treatment are clearly activated, leading to the appearance of

radicals with smaller line width, higher g-values and less relaxation pathways. Lignin contains radicals which are stabilized by its aromatic units. First steps of lignin degradation (demethoxylation, β -O-4 bond cleavage) could lead to an increase in such radicals. The appearance at 230 °C of new aromatic units observed by NMR could be correlated to the increase and change in shape or properties of the radical EPR signal. The huge increase of radical concentration at 300 °C could be tentatively related to the disappearance of the cell wall integrity, which is commonly observed in this range of temperature [33].

4. Discussion

Fig. 8 gives an overview of the main results gathered in this work. As expected, the different wood polymers do not have the same reactivity over the temperature range considered here. Cellulose is the most thermally stable component, while hemicelluloses and lignin degradation are reported to begin just above 200 °C. These conclusions are supported by data from the literature, based on thermo gravimetric analyses (TGA) investigations on isolated components: the activation energies are 150–160 kJ mol^{-1} for hardwood lignin [34], 168 kJ mol^{-1} for xylan [35] and 244 kJ mol^{-1} for cellulose [36]. It should be mentioned that these results have to be considered with care, since several parameters seem to affect the data: nature of the biomass, protocol used to extract the polymers, in particular for lignin, [34], kinetic parameters obtained with single or multi heating rate experiments, etc. Furthermore, the thermal degradation behaviour of the individual polymers of wood probably differs from the one observed in their interacted structure as found in wood itself. In particular, the release of acetic acid and elevated temperatures can give rise to acidic hydrolysis of polysaccharides and lignin, and then enhance the decomposition of the material [7,13].

In this work, lignin appears to be one of the first polymer which is thermally affected. Demethoxylation of syringyls is the first reaction observed when the temperature of torrefaction rises above 200 °C. As a matter of fact, Fig. 5d shows that there is already a slight evolution of the signals corresponding to both syringyl and methoxyl groups below 200 °C. At such temperature, lignin is reported to undergo softening, which can be associated with some weight loss [37]. This could explain the slight weight loss of 0.2% observed for the wood sample treated at 200 °C, provided it is significant. However, bulk lignin polymers remain quite stable since no significant cleavage of β -O-4 structures can be detected up to 245 °C. The low water content in the gas phase produced during the treatment probably explains the resistance of these structures. The stability of β -O-4 structures can appear surprising since they have been shown to be very labile in steam explosion treatments.

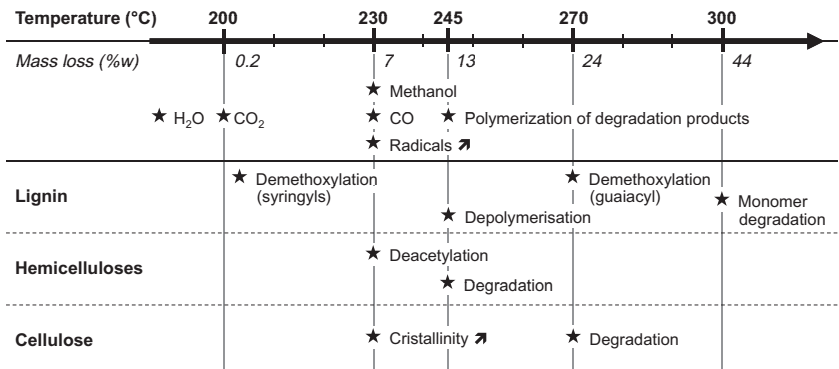


Fig. 8. Overview of mass losses, produced volatiles and transformations of the wood polymers as a function of the torrefaction temperature. Stars indicate temperatures at which the processes are clearly observed in the different measurements.

However it has to be recalled that the water content in the surrounding of wood is very large in steam explosion. This leads for instance to the formation of acetic acid at the beginning of the treatment which induces acidic hydrolyses of the β -O-4 structures. Such conditions are not encountered in torrefaction, all the more so as the treatment itself favours water elimination. Based on the results presented in Fig. 5a, hemicelluloses undergo drastic transformations above 200 °C as well. Cellulose molecular organisation on its side changes when the wood is heated above 250 °C, with first an increase of the crystalline cellulose proportion between 200 and 245 °C. As expected, cellulose degradation occurs at higher torrefaction temperatures, from 270 °C on, as shown in Fig. 8.

On a morphological point of view, our results based on chemical analyses are consistent with the expected degradation of the cell wall and the disappearance of the middle lamellae. However, based on microscopy studies [33] depletion of middle lamellae is generally reported as an important step in the degradation of the cell wall in wood heated at temperatures around 300 °C. Contrarily to lignin, which is the main component of wood middle lamellae, hemicelluloses and cellulose are the wood components that define the morphological features of the cell wall and allow its morphological observation using microscopy. Our results strongly suggest that the “disappearance” of the middle lamellae that has been described around 300 °C rather results from a morphological consequence of the degradation of hemicelluloses and cellulose in the cell wall where mainly lignin aromatic structures and products of sugar degradation remain. In other words, disappearance of the cell wall itself would be more a more accurate description that disappearance of middle lamellae due to lignin depletion.

New aromatic and aliphatic signals occurring in the spectra of torrefied woods originate from the breaking of molecules in the material. Their occurrence and their relative intensities are thus representative of the effect of the thermal treatment on the constituting polymers, as are the yields of volatile compounds and the amount of free radicals in the material. From the respective evolution of these new aromatic and aliphatic signals as a function of the torrefaction temperature (Fig. 9), it can be deduced that the process of degradation starts to be significant for heat treatments above 230 °C. This is confirmed by the evolution of the weight losses (see Fig. 8). Even though lignin degradation has been found to start below 230 °C, and the first volatile products of the reaction, mainly CO₂ and H₂O, are measured as soon as the treatment temperature exceeds 200 °C, the extent of wood-polymers degradation is very limited for a torrefaction temperature ranging from 200 to 230 °C.

As part of the volatiles could not be measured in this study, it is difficult to make a complete link between molecular degradation and the release of volatiles. Nevertheless, on the basis of the data collected here, some information can be extrapolated. NMR investigations have shown that the thermal treatment induces demethoxylation of the lignin molecules, which could further yield formic acid or methanol as volatiles. The yield of methanol by thermal degradation of lignin is already mentioned by [38,12]. Hemicelluloses thermal degradation is reported to yield in particular acetic acid, but also formic acid, formaldehyde and furfural [7,12,38]. Here, the breaking of acetyl groups is observed in the NMR spectra, which is expected to generate acetic acid. Furthermore, the evolution of the hemicelluloses degradation as a function of the torrefaction temperature appears to be a regular mechanism as shown from the CPMAS ¹³C NMR results. In particular, the two-step mechanism classically admitted for xylan decomposition [11], with a second step starting above 270 °C, has not been detected in this study.

As already mentioned, cellulose is the most stable wood component, and our investigations have confirmed this tendency. Before degradation, cellulose organisation is modified by the thermal

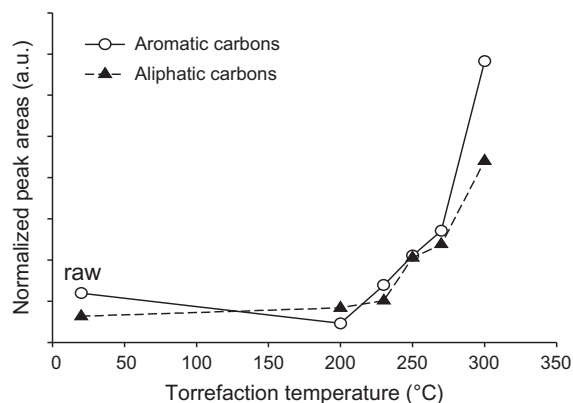


Fig. 9. Evolution of the signals corresponding to new aromatic and aliphatic carbons (broad signals centred at 128 and 32 ppm, respectively) produced by the heat treatment as a function of the torrefaction temperature. Points at 20 °C (labelled “raw”) correspond to the reference dried raw wood.

treatment, which should have an effect on the mechanical properties of the material. The gap observed for torrefaction temperatures between 270 °C and 300 °C, both on the evolution of the mass losses (Fig. 8) and on the van Krevelen diagram (Fig. 2b), could be attributed to molecular cellulose degradation. As soon as the temperature threshold of the thermal decomposition of cellulose is exceeded, the molecular reactions should yield acetic and formic acid, water, and other volatiles [38].

5. Conclusions

In this study, the effect of torrefaction on wood samples has been investigated by ¹³C NMR and EPR spectroscopies. These techniques gave access to molecular transformations occurring within the three major polymers constituting the material (cellulose, hemicelluloses and lignin). Both qualitative and semi-quantitative results were obtained. The main chemical changes in the different polymers of wood were identified and an evolution of the cellulose organisation with the thermal treatment revealed. In particular, the analysis presented here allowed identification for each wood constituent of the threshold temperatures at which degradation occurs on the molecular level, under the treatment conditions considered (duration of the treatment, neutral atmosphere). Therefore these results give an indication for the minimal temperature that should be used to impair the structure of wood major constituents. This study will be completed with further investigations on different types of biomasses, with various nature and proportions of constituting polymers. Additional NMR experiments could also give access to wider information, in particular to quantitative results.

References

- [1] Hofbauer H. Technology overview. In: Bridgwater AV, Hofbauer H, van Loo S, editors. Thermal biomass conversion. CPL Press; 2009.
- [2] Bergman P, Boersma A, Kiel J, Prins M, Ptasinski K, Janssen F. Torrefaction for entrained flow gasification of biomass. Petten: Energy Research Centre of Netherlands; 2005.
- [3] Svoboda K, Pohorely M, Hartman M, Martinec J. Pretreatment and feeding of biomass for pressurized entrained flow gasification. Fuel Process Technol 2009;90:629–35.
- [4] Arias B, Pevida C, Feroso J, Plaza MG, Rubiera F, Pis JJ. Influence of torrefaction on the grindability and reactivity of woody biomass. Fuel Process Technol 2008;89:169–75.
- [5] Bridgeman TG, Jones JM, Williams A, Waldron DJ. An investigation of the grindability of two torrefied energy crops. Fuel 2010;89:3911–8.
- [6] Tjeerdma BF, Boonstra M, Pizzi A, Tekely P, Militz H. Characterisation of thermally modified wood: molecular reasons for wood performance improvement. Holz Als Roh-Und Werkstoff 1998;56:149–53.

- [7] Weiland JJ, Guyonnet R. Study of chemical modifications and fungi degradation of thermally modified wood using DRIFT spectroscopy. *Holz Als Roh-Und Werkstoff* 2003;61:216–20.
- [8] Hakkou M, Petrissans M, Zoulalian A, Gerardin P. Investigation of wood wettability changes during heat treatment on the basis of chemical analysis. *Polym Degrad Stabil* 2005;89:1–5.
- [9] Metsä-Kortelainen S, Antikainen T, Viitaniemi P. The water absorption of sapwood and heartwood of Scots pine and Norway spruce heat-treated at 170 degrees C, 190 degrees C, 210 degrees C and 230 degrees C. *Holz Als Roh-Und Werkstoff* 2006;64:192–7.
- [10] Prins MJ, Ptasiński KJ, Janssen F. Torrefaction of wood – part 1: weight loss kinetics. *J Anal Appl Pyrolysis* 2006;77:28–34.
- [11] Di Blasi C, Lanzetta M. Intrinsic kinetics of isothermal xylan degradation in inert atmosphere. *J Anal Appl Pyrolysis* 1997;40–41:287–303.
- [12] Weiland JJ, Guyonnet R, Gibert R. Analysis of controlled wood burning by combination of thermogravimetric analysis, differential scanning calorimetry and Fourier transform infrared spectroscopy. *J Therm Anal Calorim* 1998;51:265–74.
- [13] Bourgois J, Guyonnet R. Characterization and analysis of torrefied wood. *Wood Sci Technol* 1988;22:143–55.
- [14] Manninen AM, Pasanen P, Holopainen JK. Comparing the VOC emissions between air-dried and heat-treated Scots pine wood. *Atmos Environ* 2002;36:1763–8.
- [15] Bardet M, Hediger S, Gerbaud G, Gambarelli S, Jacquot JF, Foray MF, et al. Investigation with C-13 NMR, EPR and magnetic susceptibility measurements of char residues obtained by pyrolysis of biomass. *Fuel* 2007;86:1966–76.
- [16] Sivonen H, Maunu SL, Sundholm F, Jamsa S, Viitaniemi P. Magnetic resonance studies of thermally modified wood. *Holzforschung* 2002;56:648–54.
- [17] Inari GN, Mounguengui S, Dumarcay S, Petrissans M, Gerardin P. Evidence of char formation during wood heat treatment by mild pyrolysis. *Polym Degrad Stabil* 2007;92:997–1002.
- [18] Dixon WT, Schaefer J, Sefcik MD, Stejskal EO, McKay RA. Total suppression in CPDAS C-13 NMR. *J Magn Reson* 1982;49:341–5.
- [19] Opella SJ, Frey MH. Selection of nonprotonated carbon resonances in solid-state nuclear magnetic resonance. *J Am Chem Soc* 1979;101:5854–6.
- [20] Pines A, Gibby MG, Waugh JS. Proton-enhanced NMR of dilute spins in solids. *J Chem Phys* 1973;59:569–90.
- [21] Massiot D, Fayon F, Capron M, King I, Le Calve S, Alonso B, et al. Modelling one- and two-dimensional solid-state NMR spectra. *Magn Res Chem* 2002;40:70–6.
- [22] Bielecki A, Kolbert AC, Levitt MH. Frequency-switched pulse sequences-homonuclear decoupling and dilute spin NMR in solids. *Chem Phys Lett* 1989;155:341–6.
- [23] Fung BM, Khitrin AK, Ermolaev K. An improved broadband decoupling sequence for liquid crystals and solids. *J Magn Reson* 2000;142:97–101.
- [24] Bridgeman TG, Jones JM, Shield I, Williams PT. Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. *Fuel* 2008;87:844–56.
- [25] Bardet M, Emsley L, Vincendon M. Two-dimensional spin-exchange solid-state NMR studies of C-13-enriched wood. *Solid State Nucl Magn Reson* 1997;8:25–32.
- [26] Gil AM, Neto CP. Solid-state NMR studies of wood and other lignocellulosic materials. In: *Annual reports on NMR spectroscopy*, vol. 37; 1999, p. 75–117.
- [27] Mannu SL. NMR studies of wood and wood products. *Prog Nucl Magn Reson Spectrosc* 2002;40:151–74.
- [28] Bardet M, Gerbaud G, Giffard M, Doan C, Hediger S, Le Pape L. 13C high-resolution solid-state NMR for structural elucidation of archaeological woods. *Prog Nucl Magn Res Spectrosc* 2009;55:199–214.
- [29] Baccile N, Laurent G, Babonneau F, Fayon F, Titirici MM, Antonietti M. Structural characterization of hydrothermal carbon spheres by advanced solid-state MAS C-13 NMR investigations. *J Phys Chem C* 2009;113:9644–54.
- [30] Solum MS, Pugmire RJ, Jagtoyen M, Derbyshire F. Evolution of carbon structure in chemically activated wood. *Carbon* 1995;33:1247–54.
- [31] Wooten JB, Seeman JL, Hajaligol MR. Observation and characterization of cellulose pyrolysis intermediates by C-13 CPDAS NMR, a new mechanistic model. *Energy Fuels* 2004;18:1–15.
- [32] Paris O, Zollfrank C, Zickler GA. Decomposition and carbonisation of wood biopolymers – a microstructural study of softwood pyrolysis. *Carbon* 2005;43:53–66.
- [33] Triantafyllou M, Papachristodoulou P, Pournou A. Wet charred wood: a preliminary study of the material and its conservation treatments. *J Archaeol Sci* 2010;37:2277–83.
- [34] Jiang GZ, Nowakowski DJ, Bridgwater AV. A systematic study of the kinetics of lignin pyrolysis. *Thermochim Acta* 2010;498:61–6.
- [35] Fisher T, Hajaligol M, Waymack B, Kellogg D. Pyrolysis behavior and kinetics of biomass derived materials. *J Anal Appl Pyrolysis* 2002;62:331–49.
- [36] Gronli M, Antal MJ, Varhegyi G. A round-robin study of cellulose pyrolysis kinetics by thermogravimetry. *Ind Eng Chem Res* 1999;38:2238–44.
- [37] Gaur S, Reed TB. Thermal data for natural and synthetic fuels. New York: Marcel Dekker Inc Publisher; 1998.
- [38] Repellin V. Optimisation des paramètres durée et température d'un traitement thermique du bois. Modifications des propriétés d'usage du bois en relation avec les modifications physico-chimiques et ultrastructurales occasionnées par le traitement thermique. In: *Phd*, Saint-Etienne University, Saint-Etienne; 2006.